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Journal of Photochemistry and Photobiology A: Chemistry 104 (1997) 35–37

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

One-photon reduction of Sm^{3+} to Sm^{2+}

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Received 10 October 1996; accepted 19 January 1997

Abstract

The photoreduction mechanism of Sm^{3+} to Sm^{2+} was studied using a KrF excimer laser. Reduction occurred via a one-photon process (different from previous suggestions). The reduction yield was 0.34 ± 0.09 in a methanol solution of 18-crown-6 with Sm^{3+}. The oxidized solvent ($^{\bullet}CH_2OH$ radical) was observed in the transient spectrum. © 1997 Elsevier Science S.A.

Keywords: One-photon reduction; Photoreduction of Sm^{3+}; Photoreduction yield; Transient absorption spectrum of Sm^{2+}

1. Introduction

Lanthanide ions in solution display broad and sharp absorption bands in the UV and near-UV to near-IR spectral regions respectively [1]. The former bands are called charge transfer (CT) or 5d ← 4f transition bands. The latter are due to inner f-shell transitions (f′ ← f transitions). Although a single photon in the visible region excites the f′ ← f transition of these ions, only luminescence is observed and no photoredox reaction can be induced. Direct excitation of the CT or 5d ← 4f transition bands has been found to induce the photoredox reactions of some lanthanide ions, including Ce^{3+}, Eu^{3+} and Sm^{3+} [1,2]. Furthermore, the photoreduction of Eu^{3+} takes place via an f′ ← f transition band by two-photon excitation [3].

There are few reports on the photoreduction of Sm^{3+} to Sm^{2+} because the photoproduct, Sm^{2+}, is unstable in solution [4,5]. Donohue [4] added a macrocyclic ether, 18-crown-6, to the solution to stabilize Sm^{2+}, and suggested that the photoreduction of Sm^{3+} to Sm^{2+} was induced by a multiphoton process. In this work, the transient absorption spectrum of Sm^{2+} has been measured by nanosecond laser flash photolysis to clarify the photoreduction process of Sm^{3+} to Sm^{2+} in more detail. The linear dependence of the concentration of Sm^{2+} on the laser fluence indicates that the photoreduction of Sm^{3+} to Sm^{2+} in solution occurs via a one-photon process.

2. Experimental details

2.1. Apparatus

The experimental system in this study consists of a KrF excimer laser (Lambda Physik, EMG 201), with a typical pulse width of 30 ns (full width at half-maximum, FWHM) and a power of 200 mJ per pulse, a pulsed Xe lamp (Tokyo Instruments, EG&G FX-265) and/or continuous wave (cw) Xe lamp (Hamamatsu, L2193), a monochromator (Jobin Yvon, H10UV), a photomultiplier (Hamamatsu, R636-10), a digital storage oscilloscope (Tektronix, 2440) and a personal computer (NEC, 9801UV). The absorption spectrum of Sm^{2+} some time after laser irradiation was measured by a spectrophotometer (JASCO, Ubest-50).

2.2. Sample

A sample containing a concentration of 0.01 M Sm^{3+} was prepared by adding a slightly stoichiometric excess of 18-crown-6 (Wako) to a methanol solution of $SmCl_3 \cdot 6H_2O$ (Wako, 99.5%). It was completely degassed by freeze–pump–thaw cycles on a high vacuum line to avoid oxidation of Sm^{2+} by dissolved oxygen. The flash photolysis measurements were carried out at room temperature.

2.3. Quantum yield

The reduction yield of Sm^{3+} (ϕ) can be determined by comparing the absorbance of Sm^{2+} with that of a standard sample under the same irradiation conditions

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PII S1010-6030(97)00021-X

$$\phi = \frac{\phi_{ref}\epsilon_{ref}A_{Sm}}{\epsilon_{Sm}A_{ref}} \qquad (1)$$

where ϕ_{ref} and ϵ_{ref} are the quantum yield and extinction coefficient respectively of the reference sample, A_{Sm} and A_{ref} are the absorbances of Sm^{2+} and a reference sample respectively under the same laser fluence and ϵ_{Sm} is the molar extinction coefficient of the Sm^{2+} ion. In methanol, its value was assumed to be the same as that in aqueous solution, i.e. 400 M^{-1} cm^{-1} at 570 nm [6]. The reference sample was naphthalene in cyclohexane solution. The $T_n \leftarrow T_1$ absorption band of naphthalene has an extinction coefficient of 24 100 M^{-1} cm^{-1} at 414 nm with a yield of 0.75 [7,8].

3. Results and discussion

3.1. Transient spectrum of Sm^{2+}

The CT bands of lanthanide ions have been discussed in detail [9]. The CT band of Sm^{3+} in aqueous solution appears in the vacuum UV region and that of Sm^{3+} in methanol solution shifts to the UV region. In the absorption spectrum, the maximum at 220 nm is assigned to the CT band from the counterion (Cl^-) to Sm^{3+}, with a molar extinction coefficient of 550.8 M^{-1} cm^{-1} [9]. This absorption band suggests that a KrF excimer laser can be employed as the light source to excite the CT band.

The transient absorption spectrum of Sm^{2+} after laser irradiation is shown in Fig. 1. The time profiles of Sm^{2+} formation after laser irradiation are also given in Fig. 1, where the photoreduction rate of Sm^{3+} to Sm^{2+} is seen to be shorter than the laser pulse width (30 ns). The filled circles and full line in the main figure show the transient absorption spectrum 100 ns after the peak of the laser pulse and the absorption spectrum of Sm^{2+} in methanol solution respectively. The latter spectrum was measured using a spectrophotometer some time after laser irradiation and is in agreement with the results of Donohue [4]. These spectra are in agreement in the region between 350 and 650 nm. However, a difference is observed below 350 nm. This phenomenon can be attributed to the absorption of oxidized methanol ($^{\bullet}CH_2OH$ radical), produced by laser irradiation according to Eq. (4) (see Section 3.3). The $^{\bullet}CH_2OH$ radical exhibits an absorption spectrum below 350 nm, and the lifetime of the radical under degassed conditions is of the order of 10^{-6} s [10]. Fig. 2 shows the absorption spectrum 3 ms after laser irradiation. It is clear that the transient spectrum does not include the absorption of the $^{\bullet}CH_2OH$ radical and is in agreement with the absorption spectrum of Sm^{2+}. The absorption intensity of Sm^{2+} at 3 ms has decreased to 20% of that at 100 ns. The decrease is due to the diffusional loss of Sm^{2+} from the monitoring region.

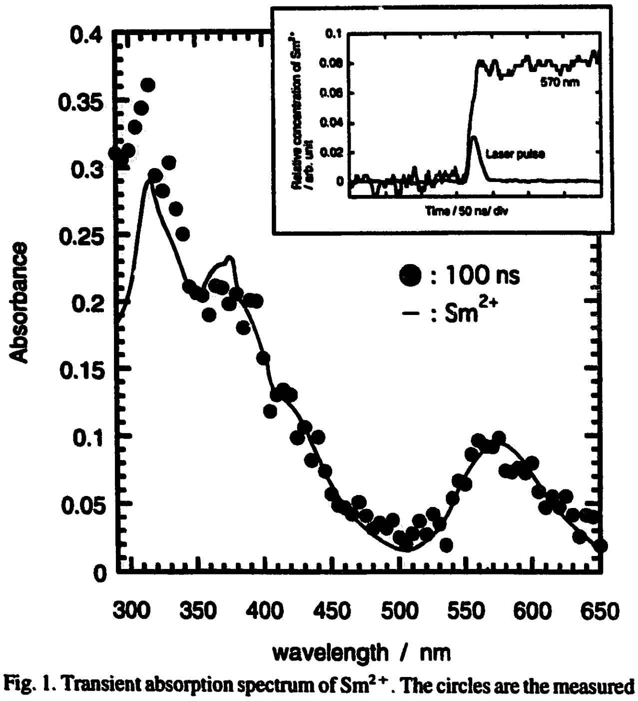

Fig. 1. Transient absorption spectrum of Sm^{2+}. The circles are the measured absorbances 100 ns after KrF laser irradiation. The full line is the absorption spectrum of Sm^{2+} in methanol. The inset shows the time profiles of Sm^{2+} formation and the laser pulse.

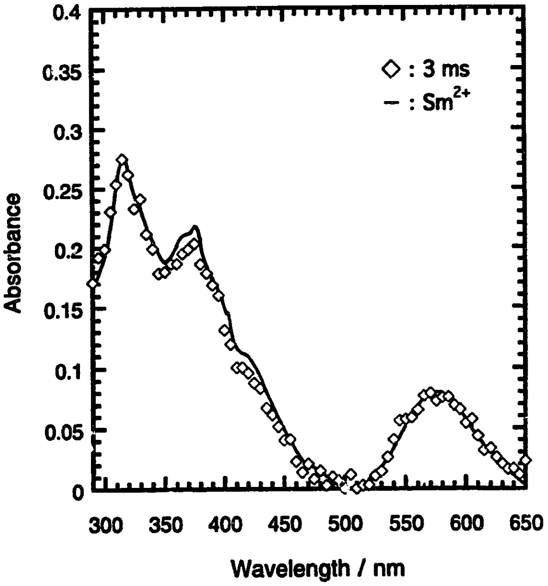

Fig. 2. Transient absorbance of Sm^{2+} 3 ms after laser irradiation (circles). The full line is the absorption spectrum of Sm^{2+}.

3.2. Laser fluence dependence

The relationship between the absorbance of Sm^{2+} at 570 nm and the KrF laser fluence is shown in Fig. 3. Absorbances were plotted 100 ns after laser irradiation. They are on a line with a slope of unity. In the previous work of Donohue [4], a multi-photon process for the photoreduction of Sm^{3+} was suggested from the improved measurement with laser irradiation instead of an Hg lamp. However, the result in this study clearly indicates that the photoreduction of Sm^{3+} to Sm^{2+} is induced by a one-photon process.

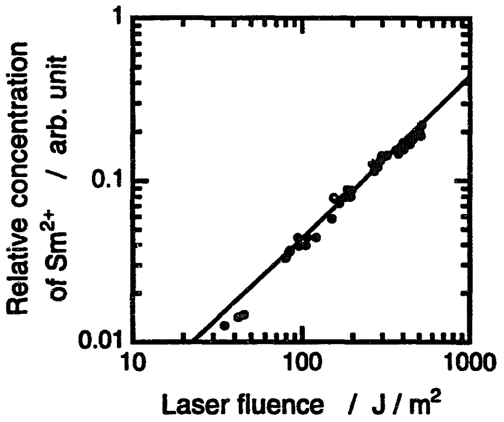

Fig. 3. Laser fluence dependence of the Sm^{2+} concentration. Absorbances were observed 100 ns after laser irradiation. The slope is unity.

3.3. Photoreduction mechanism of Sm^{3+} to Sm^{2+}

The photoreduction yield of Sm^{3+} was determined to be 0.34 ± 0.09 by Eq. (1) described in Section 2.3. The yield of Sm^{3+} to Sm^{2+} can be explained through the reaction process as follows. As soon as a photon is absorbed in the CT band due to the CT transition from Cl^- to Sm^{3+}, a geminate pair $(Sm^{2+}\text{–}Cl)^*$ is formed, and dissociates to Sm^{2+} + ·Cl. These processes are shown below.

$$Sm^{3+}-Cl^- + h\nu \rightarrow (Sm^{2+}\text{–}Cl)^* \qquad (2)$$

$$(Sm^{2+}\text{–}Cl)^* \rightarrow Sm^{2+} + {}^{\bullet}Cl \qquad (3)$$

The photoreduction yield of Sm^{3+} to Sm^{2+} will be determined by the efficiencies of dissociation and geminate recombination of the excited species. Reaction between the oxidized ligand (·Cl) and the neighbouring solvent competes with geminate recombination. In methanol solution, ·Cl reacts very efficiently with the surrounding methanol and the $^{\bullet}CH_2OH$ radical is produced following Eq. (4)

$${}^{\bullet}Cl + CH_3OH \rightarrow HCl + {}^{\bullet}CH_2OH \qquad (4)$$

The photoreduction yield may be influenced by the water included in the sample. It should be noted that the CT band of H_2O to Sm^{3+} in the vacuum UV region [9] cannot be excited by KrF excimer laser light. Therefore no photoreduction is expected between Sm^{3+} and the ligand H_2O.

Similar photoredox reactions can probably be observed in solutions containing other lanthanide or actinide ions where the photoproducts are unstable. The photochemistry of lanthanide and actinide ions in solution is important, because it provides useful information for the development of reprocessing and partitioning techniques for nuclear fuel and high level wastes.

Acknowledgements

We thank Mr K. Yamaoka for his assistance with this work. This work was supported financially by Institute of Laser Engineering, Osaka University and Institute for Laser Technology.

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